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PREPARATION AND PROPERTIES OF PIPERAZINE POLYSULFONAMIDES

ROBERT C. EVERS
GERHARD F. L. EHLERS

TECHNICAL REPORT AFML-TR-66-133

JUNE 1966

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

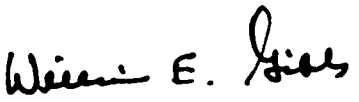
This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Dr. G. F. L. Ehlers, Project Engineer.

This report covers work conducted from August 1965 to February 1966. The manuscript was released by the authors in April 1966 for publication as an RTD Technical Report.

The authors wish to thank the Analytical Branch, Air Force Materials Laboratory, for performing the elemental analysis and molecular weight determinations.

Differential thermal analysis measurements were performed by the U. S. Rubber Company under Air Force contract.

This technical report has been reviewed and is approved.



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ABSTRACT

A series of polysulfonamides containing the piperazine moiety has been prepared by the polycondensation of piperazines or disilylpiperazines and aromatic disulfonyl chlorides. The polymers were characterized by infrared and elemental analysis, inherent viscosities, and molecular weight determinations. Their thermal behavior was evaluated by softening range determination, thermogravimetric analysis, and differential thermal analysis.

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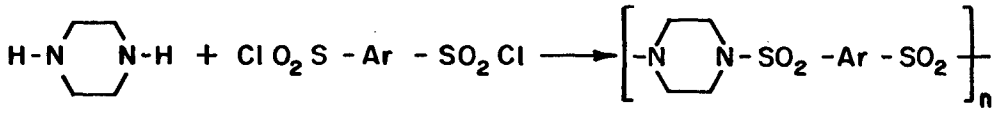
SECTION I

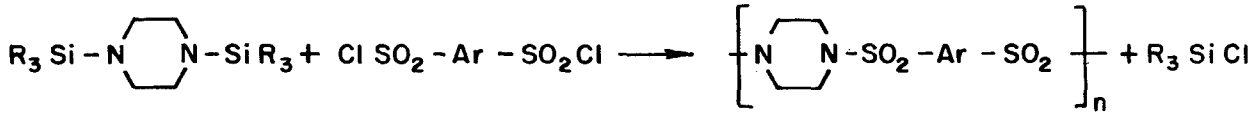
INTRODUCTION

A number of investigators have studied the polymerization of piperazines with a variety of difunctional aromatic compounds (References 1 through 10). Among these investigations was the preparation of polyamides from piperazines and aromatic diacid chlorides (References 7 and 8). These polymers were of high molecular weight and exhibited appreciable thermal stability; i.e., thermogravimetric studies in vacuo showed breakdown in the region of 420° to 480°C (References 11 and 12). An analogous system which has been only summarily investigated is that of the piperazine polysulfonamides (Reference 9). These polymers might be prepared by the polycondensation of piperazines with aromatic disulfonyl chlorides:



Kwolek used this approach in the preparation of an aromatic piperazine polysulfonamide of low molecular weight (Reference 9). Although a number of other approaches are possible, this reaction appeared to be the most promising since it was analogous to the known polycondensation of the corresponding carbonyl compounds (References 7 and 8).

Due to the difficulty generally encountered in preparing high molecular weight polysulfonamides (Reference 13), it appeared that some rather novel synthetic approaches might be in order if high molecular weight products were to be obtained. A method of possible utility was the polycondensation of disilylpiperazines with aromatic disulfonyl chlorides:



A previous investigator had reported remarkable success in obtaining high molecular weight polymers from the analogous reaction of disilylpiperazines with α, α'-dihaloxylenes (Reference 10). It was felt that such an approach might lend itself to the preparation of piperazine polysulfonamides.

Accordingly, the synthetic approaches described above were performed using standard laboratory techniques. The resulting piperazine polysulfonamides were characterized and their thermal stability evaluated.

SECTION II

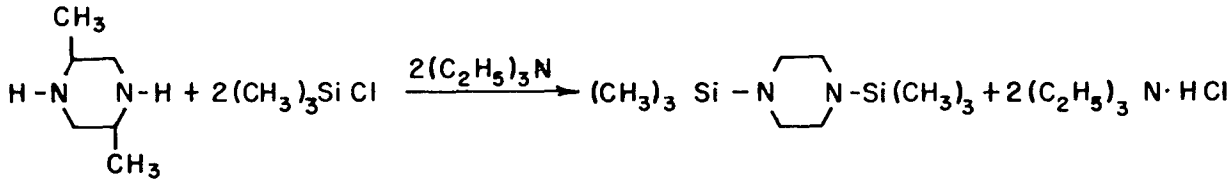
DISCUSSION

A. Preparation of Monomers

Piperazine and trans-2,5-dimethylpiperazine were obtained through commercial sources.

m-Benzenedisulfonyl chloride, diphenylether-4,4'-disulfonyl chloride and diphenylmethane-4,4'-disulfonyl chloride had been prepared in a previous investigation in the Air Force Materials Laboratory (AFML) (Reference 15).

Bis-N,N'-(trimethylsilyl)-trans-2,5-dimethylpiperazine was prepared by the reaction of chlorotrimethylsilane and trans-2,5-dimethylpiperazine with triethylamine being used as an acid acceptor (Reference 10):



B. Preparation of Polysulfonamides

Piperazine was reacted with m-benzenedisulfonyl chloride, diphenylether-4,4'-disulfonyl chloride, and diphenylmethane-4,4'-disulfonyl chloride using solution or interfacial polymerization methods. In all cases, the products were soluble only in cold sulfuric acid and exhibited low inherent viscosities in that solvent.

In order to obtain a more soluble polymer, trans-2,5-dimethylpiperazine was used as a monomer. The polycondensation of this compound with m-benzenedisulfonyl chloride was performed using methods similar to those used above. The products were soluble in a number of organic solvents but also were of low inherent viscosities.

Either a chloroform-water or a toluene-water solvent system was used in the interfacial polymerizations. The solution polymerizations were performed in a chloroform medium in a manner to that used for the corresponding polyamides. However, the polysulfonamides were insoluble in this solvent and precipitated during the course of the polymerization. It was felt that this, in part, was responsible for the low inherent viscosities of the polymers. An attempt was made to increase the molecular weight of the products by using a reaction medium in which the polymer was soluble. Dimethylsulfoxide, pyridine, and N-methyl-2-pyrollidone were used as solvents in the polymerization of trans-2,5-dimethylpiperazine and m-benzenedisulfonyl chloride. In the case of dimethylsulfoxide, the infrared spectrum, elemental analysis, and physical characteristics of the product indicated that the solvent had entered into or altered the course of the reaction. With pyridine and N-methyl-2-pyrollidone, the products obtained were similar to those obtained when chloroform was used as a reaction medium. No appreciable increase in inherent viscosity was noted.

An attempt to prepare the above polymer by the melt polycondensation of trans-2,5-dimethylpiperazine and m-benzenedisulfonyl chloride was unsuccessful. Extensive decomposition occurred during the prolonged reaction times and high temperatures (~200°C) necessary to effect the evolution of HCl.

The melt polycondensation of m-benzenedisulfonyl chloride with bis-N,N'-(trimethylsilyl)-trans-2,5-dimethylpiperazine was performed. Since the polymer was insoluble in the chlorotrimethylsilane by-product, the solubilizing effect reported in other systems (Reference 10) was not present. The reaction was repeated using tetramethylene sulfone as a reaction medium. Although the resulting polymer remained in solution, only a slight increase in inherent viscosity was recorded.

C. Properties of the Polysulfonamides

In general, the polymers were white or cream-colored powdery materials. They exhibited inherent viscosities ranging from 0.05 to 0.12. Vapor pressure osmometry molecular weight determinations gave values ranging from 1630 to 2290 for several of the trans-2,5-dimethylpiperazine polymers. These values would correspond to approximately 5 to 7 repeating units in the molecule.

The infrared spectra of the polymers were consistent with the proposed structures. In all cases, bands at 1320 to 1380 cm^{-1} and 1140 to 1180 cm^{-1}, indicative of a sulfonamide group (Reference 14), were present. Also present were bands at 2800 to 3000 cm^{-1}, attributable to aliphatic carbon-hydrogen bands, and bands at $\sim$ 1450 and $\sim$ 1600 cm^{-1}, indicative of the phenyl nucleus (Reference 14).

The softening range of the samples was obtained through use of a modified Vicat apparatus. The piperazine polymers were found to soften in the range of 250° to 280°C while the trans-2,5-dimethylpiperazine polymers softened in the range of 150° to 200°C. The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (ΔT = 150°C/hr). All the polymers show a breakdown in the region of 300° to 350°C with the polymers from the polycondensation of piperazine and m-benzenedisulfonyl chloride exhibiting the best stability. Differential thermal analysis (DTA) studies of three of the polymers revealed decomposition endotherms between 324° and 370°C. The polymer from piperazine and diphenylmethane-4,4'-disulfonyl chloride had two additional endotherms at 55° and 190°C. The latter possibly can be attributed to the melting point.

SECTION III

EXPERIMENTAL

A. Preparation of Monomers

1. Piperazine

Anhydrous piperazine was obtained from the Jefferson Chemical Company and was recrystallized from acetone, mp 106° to 108°C (Lit. 108°).

2. trans-2,5-Dimethylpiperazine

trans-2,5-Dimethylpiperazine was obtained from K and K Laboratories and was recrystallized from ligroin, mp 116° to 117°C (Lit. 118°).

3. Disulfonyl Chlorides

The various disulfonyl chlorides used in this investigation had been previously prepared in the AFML (Reference 15). Their melting points are given below:

m-benzenedisulfonyl chloride, mp 60° to 61°C (Lit. 61 to 62°)

4,4'-diphenyletherdisulfonyl chloride, mp 129°C (Lit. 129°)

4,4'-diphenylmethanedisulfonyl chloride, mp 122° to 23°C (Lit. 124°)

4. Bis-N,N' -(trimethylsilyl)-trans-2,5-Dimethylpiperazine

Into a carefully dried 300 ml, round bottom, three-necked flask fitted with a dropping funnel, a mechanical stirrer, and a reflux condenser with a drying tube was placed trans-2,5-dimethylpiperazine (5.70 g, 0.05 mole) in 150 ml of anhydrous ether. With vigorous stirring being maintained, a solution of chlorotrimethylsilane (10.86 g, 0.10 mole) was added dropwise. The mixture warmed up spontaneously and a white precipitate was formed. The reaction was stirred one hour. Then dry triethylamine (12.50 g, 0.125 mole) was added and the reaction stirred overnight. The precipitate of triethylamine hydrochloride was filtered off and the ether stripped off under reduced pressure. The residue was distilled and 5.77 g of product was obtained in 44 percent yield. A boiling point of 109°C/10 mm (Lit. 112°/11 mm) (Reference 10) was recorded.

B. Preparation of Polymers

The experimental conditions for the various polymerizations are given in Table 1. Typical preparative procedures for the polymers are as follows:

1. Interfacial Polycondensation

A solution of the piperazine (0.01 mole) in 60 ml of water was placed in a Waring Blender. Sodium hydroxide (0.02 mole) was added as an acid acceptor and sodium lauryl sulfate (0.1 g) as a surface active agent. A solution of the disulfonyl chloride (0.01 mole) in 45 ml of alcohol-free chloroform was prepared. With the blender being run at a moderate speed, the chloroform solution was added rapidly and the blender then run at full speed for thirty minutes. The polymer was precipitated by the slow addition of the reaction mixture to 300 ml of rapidly stirred acetone. After being washed with hot water, the polymer was isolated by filtration, dried in a vacuum oven, and ground into a fine powder. It was purified by extraction with methanol in a Soxlet for 48 hours and was then dried in a vacuum oven at 80°C for 24 hours.

2. Solution Polycondensation

Into a 100 ml round bottom, three-necked flask fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser with a drying tube was placed a solution of the disulfonyl chloride (0.01 mole) in 35 ml of alcohol-free chloroform. Then a solution of the piperazine (0.02 mole) in 30 ml of chloroform was added slowly. Vigorous stirring was maintained and the solution heated to reflux. A precipitate formed almost immediately. This reaction was allowed to continue for several hours at which time the reaction mixture was poured into pet ether and the precipitate isolated by filtration. It was washed well with methanol and hot water. The finely crushed polymer was extracted with methanol in a Soxlet for 50 hours and the product dried in a vacuum oven at 110°C for 24 hours.

3. Polymerization of Bis-N-N'-(trimethylsilyl)-trans-2,5-dimethylpiperazine and m-Benzenedisulfonyl Chloride

Into a 15 ml round bottom flask fitted with a nitrogen inlet and a reflux condenser with a drying tube was placed bis-N,N'-(trimethylsilyl)-trans-2,5-dimethylpiperazine (3.64 g, 0.014 mole). This transfer was carried out in a dry box. Then m-benzenedisulfonyl chloride (3.87 g, 0.014 mole) was added along with 15 ml of tetramethylene sulfone. The system was placed under a nitrogen blanket and the reaction mixture heated at 50°C for two hours. The temperature was then raised to 100°C for 22 hours. The polymer was precipitated by addition of the clear brown reaction mixture to 150 ml of methanol and isolated by filtration. It was extracted with methanol in a Soxlet for 24 hours. The polymer was dried in a vacuum oven at 110°C for 40 hours. The dried polymer (2.5 g) was obtained in 67 percent yield.

C. Physical Properties of the Polymers

1. Elemental Analysis

The elemental analysis of the polymers prepared in this investigation is presented in Table 2.

2. Viscosity

The inherent viscosities of the polymers were determined at 25°C using solution concentrations ranging from 0.2 g to 0.6 g/100 ml. The viscosities of the respective polymers are summarized in Table 3.

3. Molecular Weight Determinations

The molecular weights of several of the trans-2,5-dimethylpiperazine polymers were determined by vapor pressure osmometry. Dimethylformamide was used as a solvent. The results are shown in Table 3.

4. Infrared Spectra

Infrared spectra were obtained on all monomers and polymers by use of a Perkin-Elmer infrared recording spectrophotometer. In all cases potassium bromide pellets of the samples were used. Representative polymer spectra are shown in Figures 1 through 4.

5. Softening Range Determination

The softening range of the polymer samples was obtained by use of a modified Vicat apparatus. Heating was performed at a constant rate of 150°C/hr. The softening range was determined from a plot of temperature vs penetration. A composite plot of the polymers is shown in Figure 5.

6. Thermogravimetric Analysis (TGA)

Determinations were carried out in a nitrogen atmosphere on a modified Chevenard thermobalance using a constant heating rate of 150°C/hr. A plot of percent weight residue vs temperature was made for each polymer. A composite plot is shown in Figure 6.

7. Differential Thermal Analysis (DTA)

DTA was performed in a specially designed block in connection with an Aminco thermobalance under helium at a heating rate of 8°C/min.

TABLE I. POLYMERIZATION

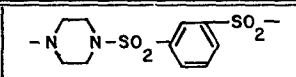
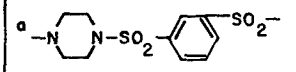
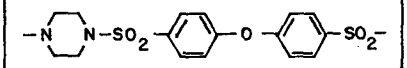
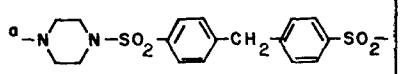
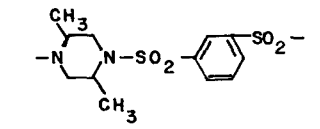
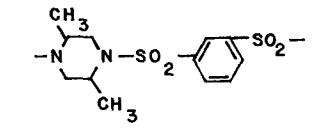
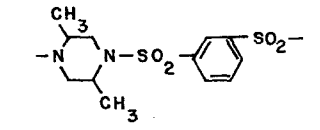
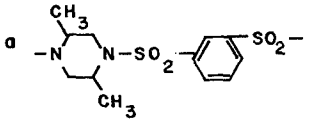
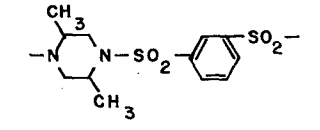
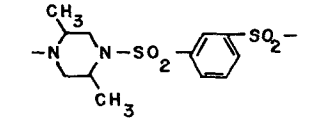
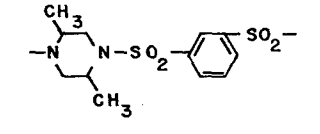
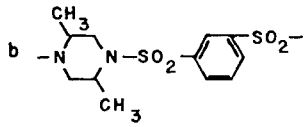
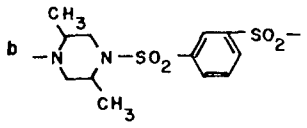
Trial No.	Structure	Reaction Medium	Acid Acceptor	Reaction Time Hrs	Reaction Temp °C	Yield %
1.		$CHCl_3$	$(C_2H_5)_3N$	0.25	room temp	73
2.	[a] 	$CHCl_3$-H_2O	NaOH	0.50	room temp	88
3.		$CHCl_3$	$(C_2H_5)_3N$	0.50	room temp	63
4.	[a] 	toluene-H_2O	piperazine	18	room temp	34
5.		$CHCl_3$	$(C_2H_5)_3N$	0.5	room temp	46
6.		$CHCl_3$	trans-2,5-dimethylpiperazine	26	60°	63
7.		$CHCl_3$	trans-2,5-dimethylpiperazine	100	60°	73
8.	[a] 	$CHCl_3$-H_2O	trans-2,5-dimethylpiperazine	18	room temp	63
9.		pyridine	pyridine	18	50° for 1 hr	27
10.		N-methyl-2-pyrollidone	N-methyl-2-pyrollidone	20	0° for 6 hrs 50° for 2 hrs	--
11.		dimethysulf-oxide	pyridine	18	80°	69

TABLE I. POLYMERIZATION CONDITIONS (Contd)

Trial No.	Structure	Reaction Medium	Acid Acceptor	Reaction Time Hrs	Reaction Temp °C	Yield %
12.	b 	melt	---	72	60° for 2 hrs 90° for 70 hrs	56
13.	b 	tetramethylene sulfone	---	24	50° for 2 hrs 100° for 22 hrs	67

a. Interfacial polymerizations
b. Polymerization of m-benzenedisulfonyl chloride and bis-N,N'-(trimethylsilyl)-trans-2,5-dimethylperazine

TABLE II. ELEMENTAL ANALYSIS

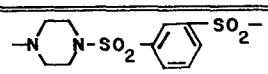
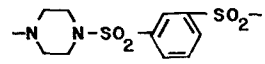
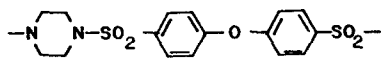
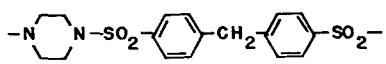
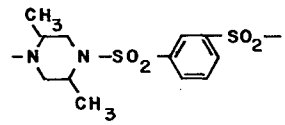
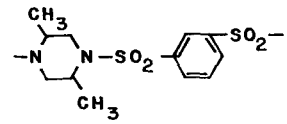
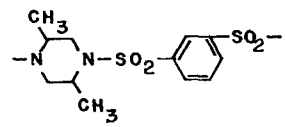
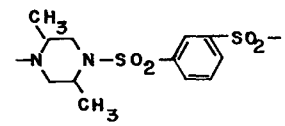
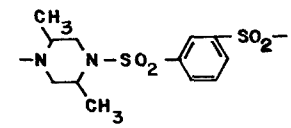
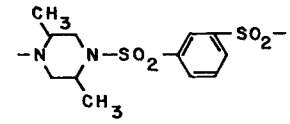
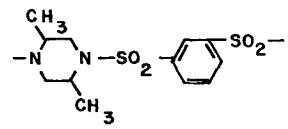
Trial No.	Structure	Calc for DP = ∞					Found				
		C	H	S	N	Cl	C	H	S	N	Cl
1.		41.7	4.2	22.2	9.8	0.0	38.7	4.5	24.3	8.7	2.1
2.		41.7	4.2	22.2	9.8	0.0	33.1	3.7	18.3	7.7	1.6
3.		50.5	4.2	16.8	7.4	0.0	49.3	4.1	15.3	7.0	0.9
4.		54.0	4.8	16.9	7.4	0.0	53.5	5.5	14.0	8.6	2.1
5.		45.6	5.1	20.3	8.9	0.0	42.2	5.5	17.7	8.9	0.3
6.		45.6	5.1	20.3	8.9	0.0	44.7	5.0	15.0	7.9	0.3
7.		45.6	5.1	20.3	8.9	0.0	45.4	5.7	18.9	8.4	1.7
8.		45.6	5.1	20.3	8.9	0.0	44.9	5.5	19.8	7.7	0.4
9.		45.6	5.1	20.3	8.9	0.0	42.3	4.9	17.5	7.4	0.4
10.		45.6	5.1	20.3	8.9	0.0	45.3	4.5	19.5	7.9	0.5
11.		45.6	5.1	20.3	8.9	0.0	48.6	8.2	16.6	6.8	0.6

TABLE II. ELEMENTAL ANALYSIS (Contd)

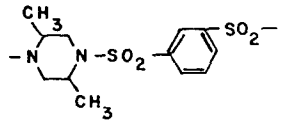
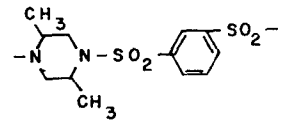
Trial No.	Structure	Calc for DP = ∞					Found				
		C	H	S	N	Cl	C	H	S	N	Cl
12.		45.6	5.1	20.3	8.9	0.0	44.6	5.3	19.4	8.2	0.8
13.		45.6	5.1	20.3	8.9	0.0	44.9	5.4	19.0	6.6	0.4

TABLE III. PHYSICAL PROPERTIES

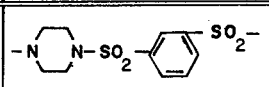
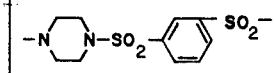
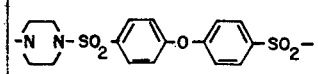
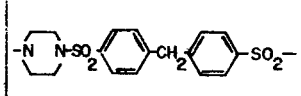
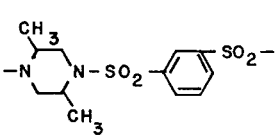
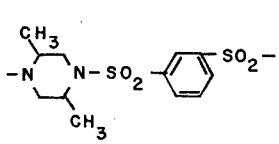
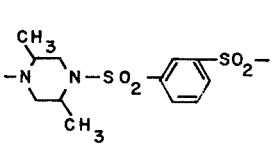
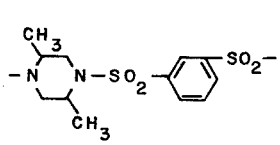
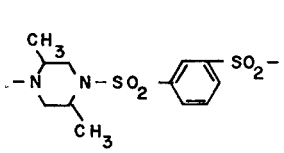
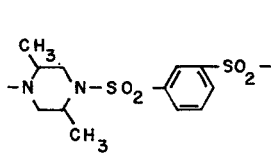
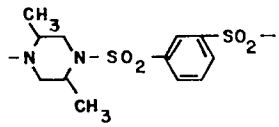
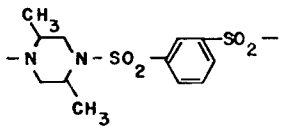
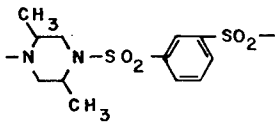
Trial No.	Structure	Appearance	Solvents	η inh (solvent)	Molecular Weight	Inversion Points (°C) Softening Curve	Inversion Points (°C) TGA Curve	DTA Transitions (°C)
1.		white powder	H_2SO_4	0.07 (H_2SO_4)	--	285	350	360
2.		white powder	H_2SO_4	0.07 (H_2SO_4)	--	-	-	-
3.		white powder	H_2SO_4	0.12 (H_2SO_4)	--	275	355	-
4.		tan powder	DMSO, DMF m-cresol, pyridine, etc.	0.06 (H_2SO_4)	--	285	355	55,190,324, 370
5.		white powder	DMSO, DMF m-cresol, pyridine, etc.	0.05 (DMSO)	--	-	-	-
6.		white powder	DMSO, DMF m-cresol, pyridine, etc.	0.07 (DMSO)	1630	180	310	235,360
7.		white powder	DMSO, DMF m-cresol, pyridine, etc.	0.07 (DMSO)	1640	-	-	-
8.		white powder	DMSO, DMF m-cresol, pyridine, etc.	0.07 (DMSO)	1660	-	-	-
9.		light green powder	DMSO, DMF m-cresol, pyridine, etc.	0.10 (DMF)	2290	-	-	-
10.		white powder	DMSO, DMF m-cresol, pyridine, etc.	0.07 (DMF)	--	-	-	-

TABLE III. PHYSICAL PROPERTIES (Contd)

Trial No.	Structure	Appearance	Solvents	η inh (solvent)	Molecular Weight	Inversion Points (°C) Softening Curve	Inversion Points (°C) TGA Curve	DTA Transitions (°C)
11.		brown powder	DMSO, DMF m-cresol, pyridine, etc.	0.06 (DMSO)	--	-	-	-
12.		tan powder	DMSO, DMF m-cresol, pyridine, etc.	0.06 (DMSO)	--	-	-	-
13.		light tan powder	DMSO, DMF m-cresol, pyridine, etc.	0.08 (DMSO)	--	-	-	-

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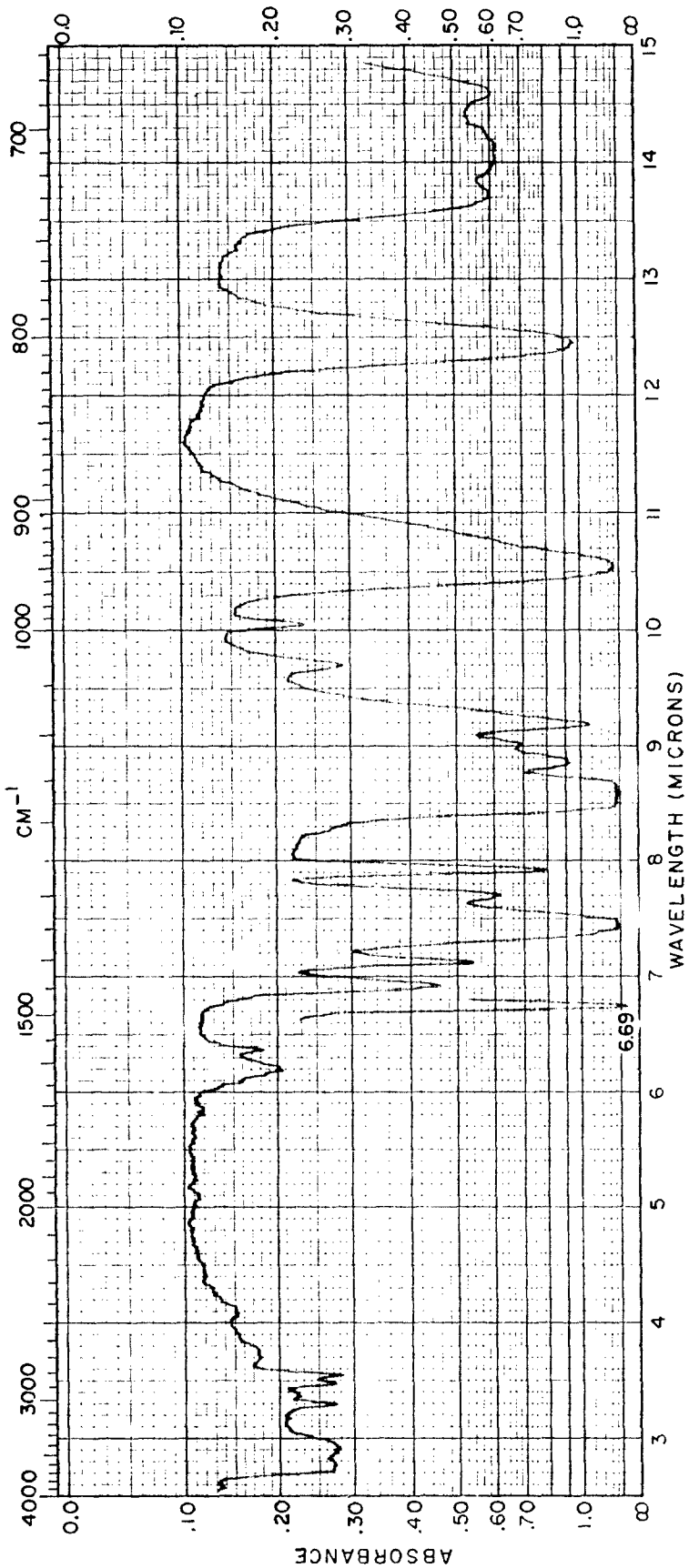

Figure 1. IR Spectrum of Polymer Prepared from Piperazine and 1,3-Benzenedisulfonyl Chloride

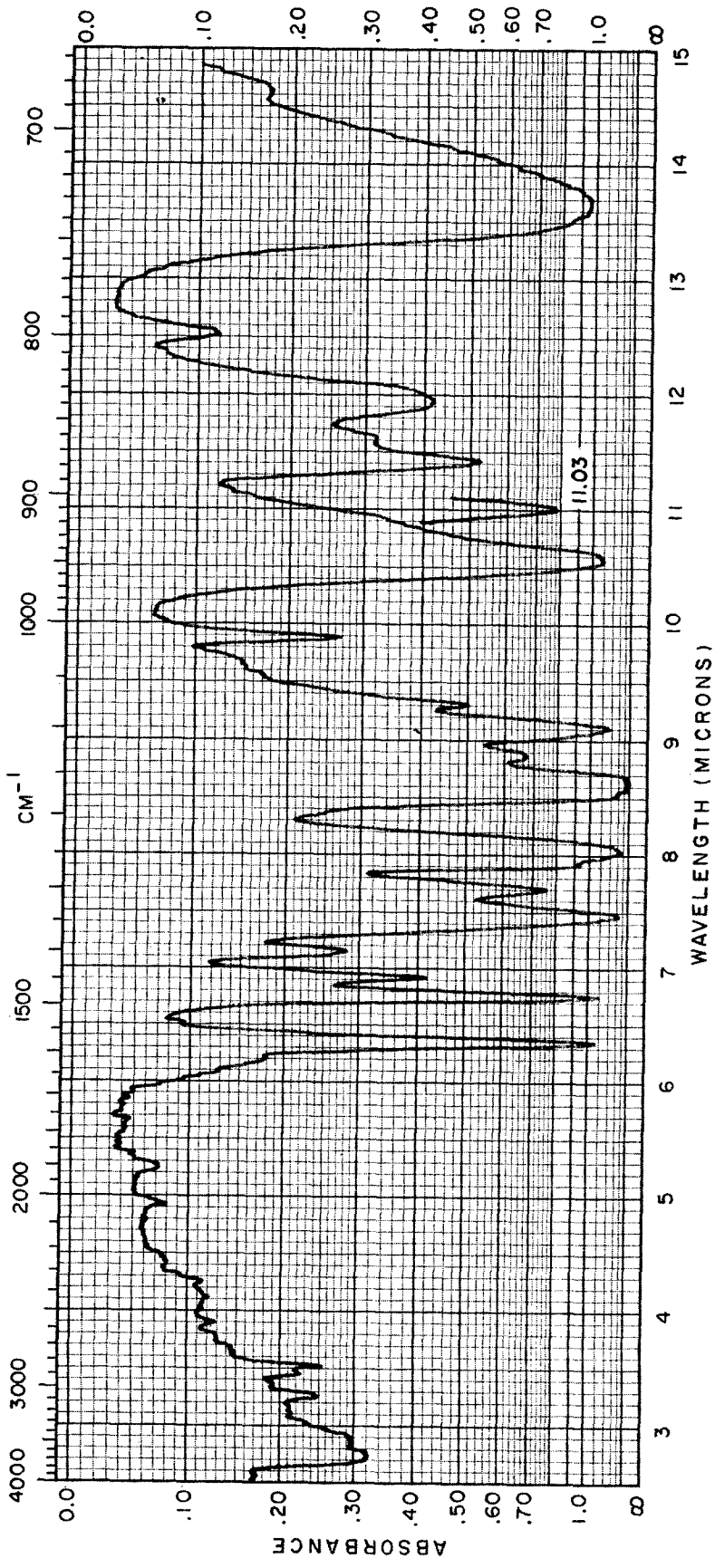

Figure 2. IR Spectrum of Polymer Prepared from Piperazine and Diphenylether-4,4'-disulfonyl Chloride

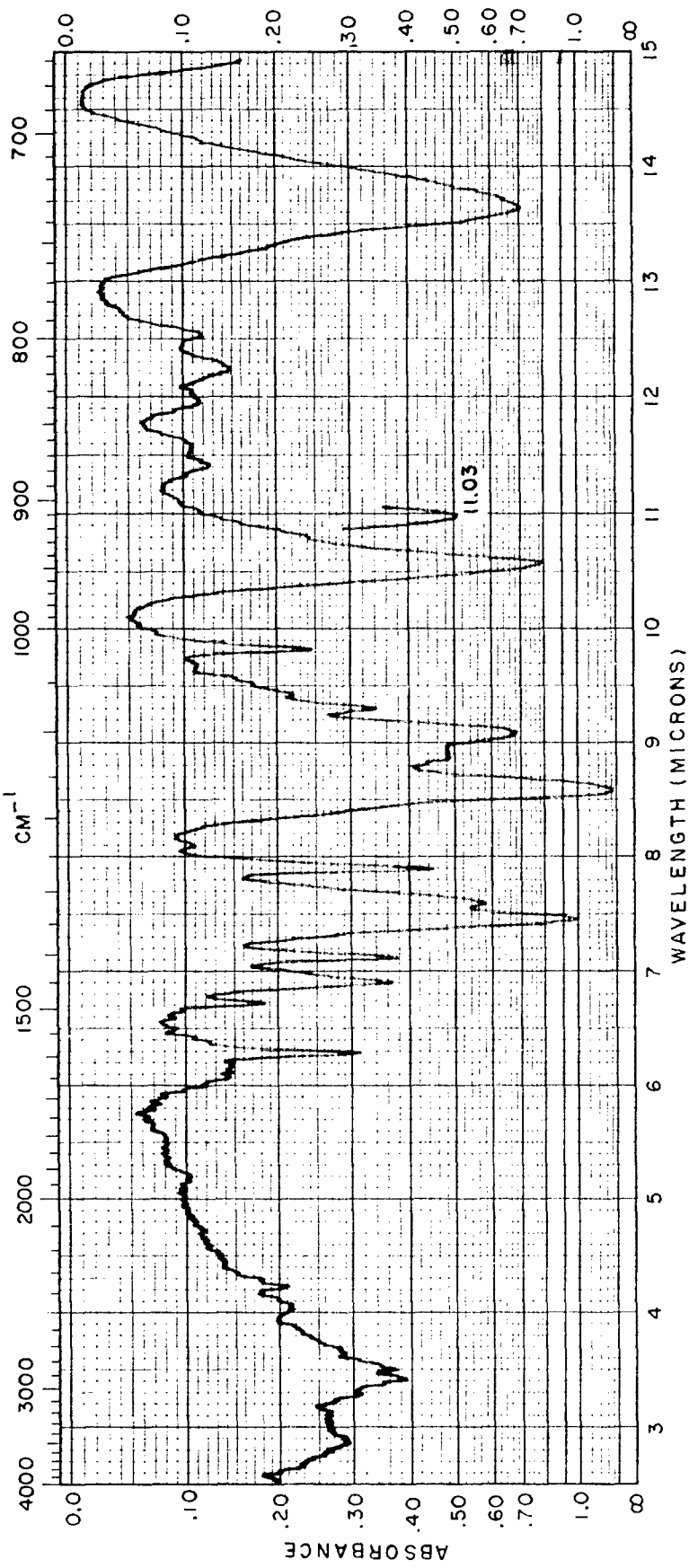

Figure 3. IR Spectrum of Polymer Prepared from Piperazine and Diphenylmethane-4,4'-disulfonyl Chloride

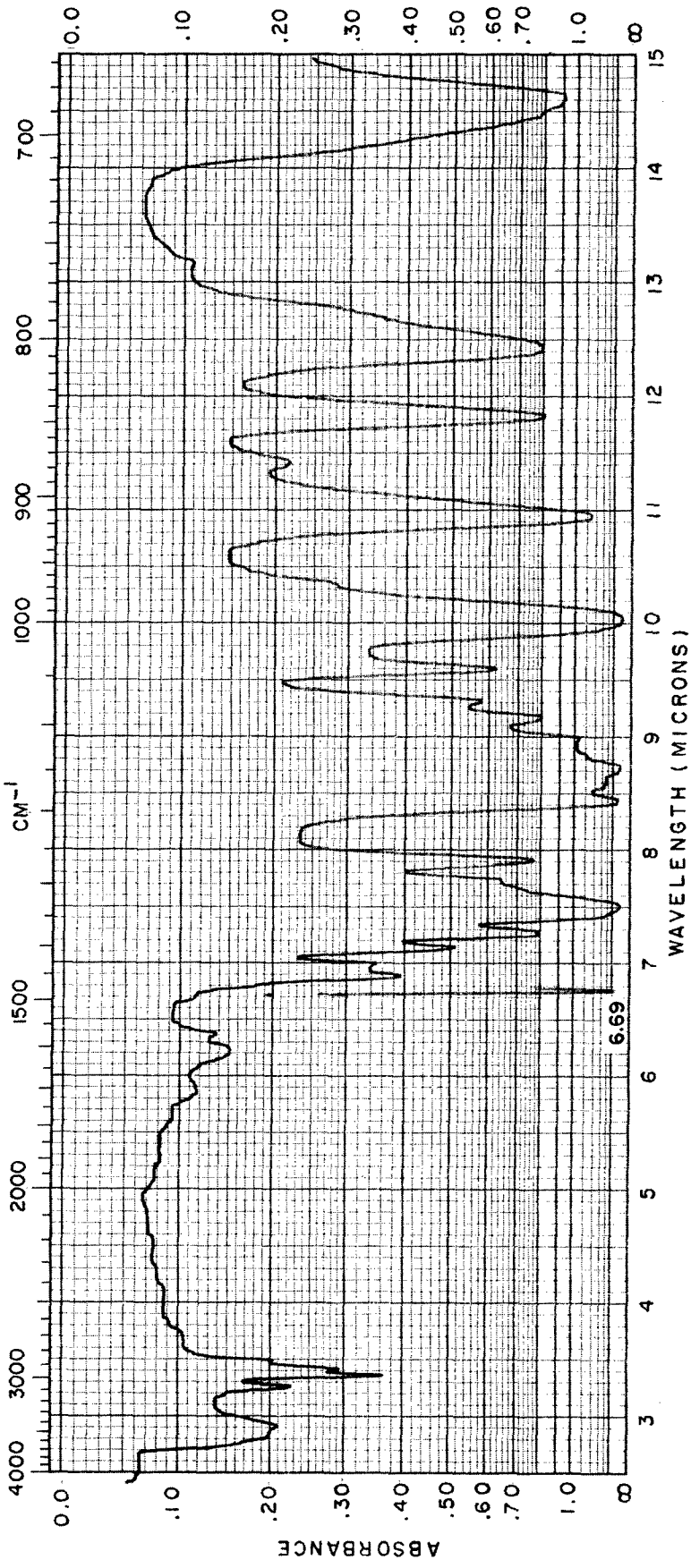

Figure 4. IR Spectrum of Polymer Prepared from trans-2,5-Dimethylpiperazine and 1,3-Benzenedisulfonyl Chloride

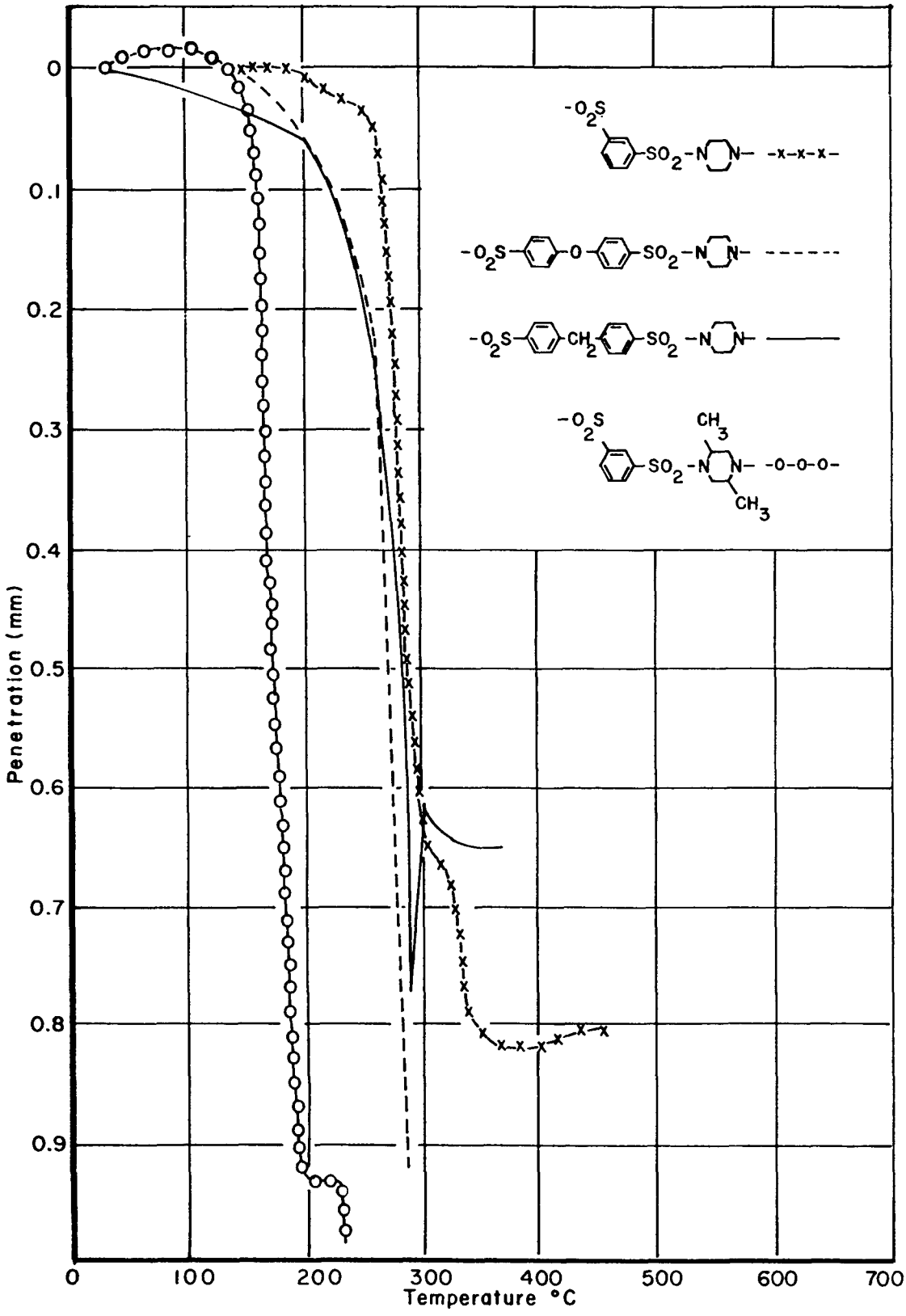

Figure 5. Composite Softening Curves Plot

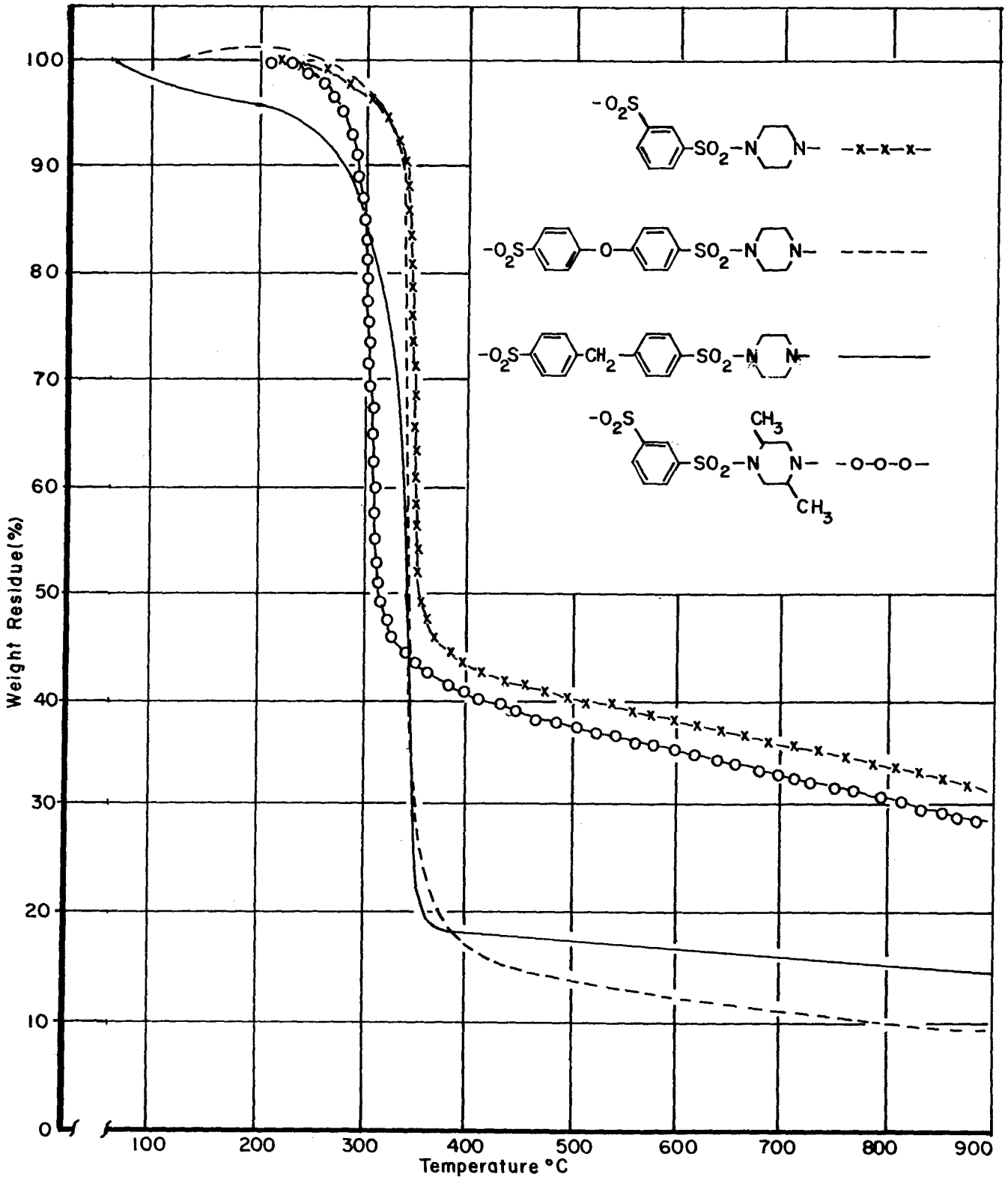

Figure 6. Composite TGA Plot

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13. ABSTRACT

A series of polysulfonamides containing the piperazine moiety has been prepared by the polycondensation of piperazines or disilylpiperazines and aromatic disulfonyl chlorides. The polymers were characterized by infrared and elemental analysis, inherent viscosities, and molecular weight determinations. Their thermal behavior was evaluated by softening range determination, thermogravimetric analysis, and differential thermal analysis.

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